CYCLODIENE PESTICIDE RESIDUES IN MOLLUSCS, CRUSTACEANS AND FISH IN THE GULF OF GDAŃSK, BALTIC SEA

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Introduction

Organochlorine cyclodiene pesticides such as chlordane and its metabolites and dieldrin are common contaminants quantified in Baltic biota (1-5). Recently also mirex was identified in the Baltic Sea environment (6, 7). Both chlordane and dieldrin were used in small quantities in the past in some of the Baltic States, while mirex was not registered. Dieldrin is known as extremely toxic compound. A very high environmental persistency and relative abundance of dieldrin in various biota from the Baltic Sea the 1990s. is a somewhat amazing (7, 9).
Chlordanes (CHLs: *trans*- and *cis*-chlordane, *trnas*- and *cis*- nonachlor, oxychlordane, heptachlor, heptachlor epoxide, MC4, MC5, MC6, MC7 and U82) aldrin, dieldrin, endrin, isodrin, endosulfan 1, endosulfan 2 and mirex were quantified in mollusc, crustacean and fishes from the Gulf of Gdańsk in order to clarify concentrations, compositional pattern, spatial distribution and possible sources of pollution.

Materials and Methods

Blue mussel (*Mytilus trossulus*), crab (*Carcinus means*) and fishes: herring (*Clupea harengus*), cod (*Gadus morhua*), pikeperch (*Stizostedion lucioperca*), perch (*Perca fluviatilis*), round goby (*Neogobius melanostomus*), sand-eel (*Hyperoplus lanceolatus*), lesser sand-eel (*Amodytes tobiasus*), lamprey (*Lampetra fluviatilis*), flounder (*Platichthys flesus*) and stickleback (*Gasterosteus aculeatus*) were collected from a several sites in the south-western part of the Gulf of Gdańsk in summer and autumn 1992 (Figure 1). A pooled samples of the soft tissues of mussel, a whole crab and fish were subjected to chemical analysis.

The analytical procedure used was a multi-residue method suitable to parallel determination of many organohalogenated compounds and polynuclear aromatic hydrocarbons (PAHs). The extraction and clean-up procedure is based on a non-destructive technology including a wide-bore glass tube elution of sodium sulphate dehydrated sample with a set of solvents, and next bulk lipid removal by means of a semipermeable polyethylene membrane (SPM) dialysis method using cyclopentane as a solvent (7, 10). A small aliquot (10%) of the extract was taken for analysis of cyclodiens and some other organochlorine pesticides and di- to tetra- *ortho* polychlorinated biphenyls (PCBs). The remaining lipid was removed on a Florisil column (35 cm length), and the analytes was fractionated using *n*-hexane (28 ml; fraction 1), methylene chloride and *n*-hexane

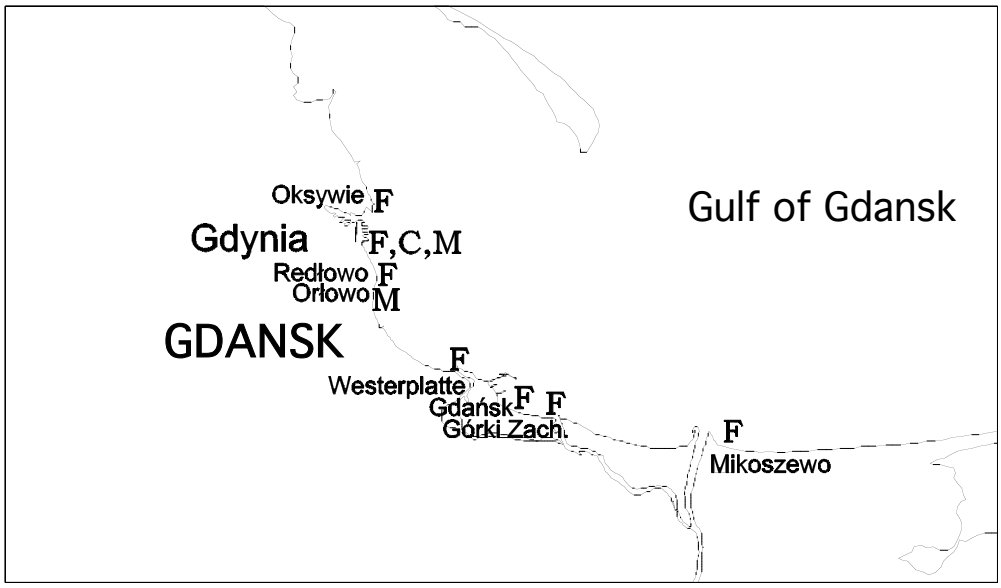

Fig. 1. Sampling sites (M., mollusc; C, crab and F, fishes).

(15:85 v/v; 38 ml; fraction 2), methylene chloride and *n*-hexane (50:50 v/v; 56 ml; fraction 3) and methanol (66 ml; fraction 4). Most of the cyclodiene pesticides were eluted in fractions 1 and 2, which were combined, while dieldrin in fraction 3 and the solvent was evaporated in room temperature with tetradecane added as a keeper. Before injection of the analytes to a capillary column gas chromatography/low resolution mass spectrometry system (HRGC/LRMS) a recovery standard of ^{13}C-2,2´,4,5,5´-pentachlorobiphenyl (PCB no. 101) was added. Procedural blanks were performed with every set of the real samples analysed, which only contained minor residues of PCBs and hexachlorobenzene and were well below 10% of any calculated value. The recoveries were generally between 60 and 120 %, and the results were corrected for recovery values.

Results and Discussion

Only chlordane compounds and their metabolites and dieldrin could be quantified in biota examined (Table 1). It was found that CHLs and dieldrin showed similar concentrations in mussels and in most of the fishes sampled.

Trans- and *cis*-chlordane, *trans*-nonachlor, oxychlordane, heptachlor epoxide, MC5 and MC7 were found in blue mussel and crab. The concentrations of CHLs and dieldrin both in blue mussel from the site Gdynia (Gdy) and Orłowo (Orł), and crab were relatively low. Chlordanes in a somewhat higher concentration then in this study were quantified recently in blue mussel sampled from the coast of Australia in 1992, *i.e.* for *cis*- and *trans*-nonachlor, *cis*-chlordane and heptachlor epoxide were between 30 and 80 ng/g lipid (11).

Dieldrin in relatively high concentration was found in *Mytilus edulis* collected from the coast of Holland in 1985-1990, *i.e.* between 100 and 300 ng/g lipid (12), while in a much higher concentration was reported in *Mytilus chilensis* sampled in La Bahia de Corral in Chile in 1990, *i.e*. 1600 ng/g lipid, and for endrin it was 2200 ng/g lipid (13).

Table 1.
The concentrations of CHLs and dieldrin in blue mussel, crab and fishes fin the Gulf of Gdańsk (ng/g lipid)

Species	No.	Lipids	CHLs	Dieldrin
Blue mussel (Gdy)	1 (350)*	1.3	12	19
Blue mussel (Orł)	1 (350)	1.7	12	11
Crab	1 (3)	1.3	41	7.6
Herring	1 (3)	9.0	49	70
Cod	1 (3)	3.4	19	51
Pikeperch	1 (3)	4.4	21	29
Perch	2 (16)	5.6	35 (28-42)	35 (28-42)
Round goby	1 (6)	4.5	17	20
Sand-eel	1 (20)	5.7	13	25
Lesser sand-eel	1 (20)	5.5	7.2	15
Lamprey	2 (6)	15	40 (24-56)	23 (17-29)
Flounder	3 (15)	4.6	18±5 (13-22)	27±4 (23-31)
Stickleback	4 (120)	2.5	84±44 (48-150)	49±19 (35-77)

Heptachlor (< 0.3 ng/g), aldrin (< 0.3 ng/g), endrin (< 0.5 ng/g), isodrin (<1.5 ng/g), endosulfan 1 and 2 (< 3 ng/g) and mirex (< 0,15 ng/g)
*Number of pooled samples and total number of animals (in parentheses)

Trans- and *cis*-chlordane, *trans*- and *cis*-nonachlor, oxychlordane, heptachlor epoxide, U82, MC4, MC5, MC6 and MC7 were quantified in all fish examined. The pattern of CHLs determined in flounder, stickleback, perch and lamprey from spatially different sites in the Gulf of Gdańsk was similar. Also similar pattern of CHLs was observed between different species of fish examined.

In earlier studies chlordane (*trans*- and *cis*-chlordane, *trans*-nonachlor and oxychlordane) was quantified in Baltic herring in concentration 520 ng/g lipid (1970), 600 ng/g lipid (1978), 560 ng/g lipid (Archipelago of Turku, 1982), 190-200 ng/g lipid (1979-87), 44 ng/g lipid (Gulf of Finland, 1985-89) and 46-96 ng/g lipid (Gulf of Bothnia, 1991) (1, 2, 6, 14, 15).

There are only a few data available on dieldrin residues in Baltic fish. In study by Jansson *et al.* (14) dieldrin content of herring in 1986-1987 was between 68 and 81 ng/g lipid, while between 36-120 ng/g lipid was reported by Strandberg *et al*. (6) in herring caught in the Gulf of Bothnia in 1991. Herring from the North Sea (Scotland, 1990-1991) contained residues of dieldrin in concentration between 52 and 140 ng/g lipid (16).

Chlordane is widely distributed in the marine ecosystems and is easily bioaccumulated and biomagnified by marine biota (17, 18). Apart from this studies CHLs in low concentration were

found in sediment from the Baltic coast of Poland in 1990 (19), and in flounder from the Gulf of Gdańsk in 1990 (3.1 ng/g wet weight) (20). A similar pattern, low concentrations and decreasing trend of CHLs quantified in fish and other matrices from the Baltic Sea did indicated that there is no fresh inputs of that pesticide. On the other hand dieldrin seems to be much more stable compound in the Baltic Sea environment.

References

1. Moilainen R, Pyysalo H, Wickström K and Linko R; *Bull. Environ. Contam. Toxicol*, 1982, 29, 334
2. Andersson Ö, Linder C-E, Olsson M, Reutergardh L, Uvemo U-B and Widequist U; *Arch. Environ. Contam. Toxicol*. 1988, 17, 755
3. Kannan K, Falandysz J, Yamashita N, Tanabe S. and Tatsukawa R; *Mar. Pollut. Bull*, 1992, 24, 358
4. Falandysz J, Kannan K, Tanabe S. and Tatsukawa R; *Ambio*, 1994, 23, 288
5. Paasivirta J; *Toxicol. Environ. Chem*. 1998, 66, 71
6. Strandberg B, Strandberg L, Bergqvist P.-A, Broman D, Falandysz J, Näf C, Papakosta O, Rolff C and Rappe C; *Sci. Total Environ*. 1998, 215, 69
7. Strandberg L, Strandberg B, Bergqvist P.-A, Rappe C and Falandysz J; *Organochlorine Compd*. 1998, 39, 453
8. Koeman JH, Bathof T, de Vries R, van Velzen-Blad H, Vos JG; *TNO-News*, 1972, 27, 561
9. Falandysz J, Strandberg B, Strandberg L, Bergqvist P.-A, Rappe C; Sci. *Total Environ. Sci. Total Environ*. 1998, 215, 253
10. Strandberg B, Bergqvist P-A and Rappe C; *Anal. Chem*. 1998, 70, 526
11. Prest HF, Richardson BJ, Jacobson LA, Vedder J, Martin M.; *Mar. Pollut. Bull*. 1995, 30, 543.
12. Stronkhorst J; *Mar. Pollut. Bull*. 1992, 24, 250.
13. Tamayo R, Ojeda H, Cristi R, Henriquez O; *Arch. Med. Vet*. 1993, 2, 181.
14. Jansson B, Andersson R, Asplund L, Litzen K, Nylund K, Sellström U, Uvemo U-B, Nahlberg K, Widequist U, Odsjö T, Olsson M.; *Environ. Toxicol. Chem*. 1993, 12, 1163.
15. Paasivirta J, Rantio T; *Chemosphere* 1991, 22, 47.
16. Kelly AG, Cambell LA; *Mar. Pollut. Bull*. 1994, 28, 103.
17. Kawano M, Inoue T, Wada T, Hidaka H and Tatsukawa R; *Environ. Sci. Technol*. 1988, 22, 792
18. Kawano M., matsushita S., Inoue T, Tanaka H, Tatsukawa R; Mar. Pollut. Bull. 1986, 17, 512.
19. Falandysz J; *Bromat. Chem. Toksykol*. 1992, 34, 387.
20. Falandysz J; *Bromat. Chem. Toksykol*. 1995, 28, 401.